chemical Institute in providing preliminary activity screening data.

Registry No.—3, 41757-95-3; **4a**, 14098-44-3; **4b**, 14187-32-7; **4c**, 14174-09-5; **5**, 67722-63-8; **6**, 67722-64-9; **7** isomer 1, 67722-65-0; **7** isomer 2, 67722-66-1; **8** isomer 1, 67722-67-2; **8** isomer 2, 67722-68-3; **9** isomer 1, 67722-69-4; **9** isomer 2, 67722-70-7; **10** isomer 1, 67722-71-8; **10** isomer 2, 67722-72-9; **13** isomer 1, 67722-73-0; **13** isomer 2, 67722-74-1; **14** isomer 1, 67722-75-2; **14** isomer 2, 67722-76-3; **15** isomer 1, 67722-77-4; **15** isomer 2, 67722-78-5; **16** isomer 1, 67722-79-6; **16** isomer 2, 67722-80-9; **20** isomer 1, 67722-81-0; **20** isomer 2, 67722 82-1; **21** isomer 1, 67722-83-2; **21** isomer 2, 67722-84-3; **24**, 67722-85-4; **25** isomer 1, 67722-86-5; **25** isomer 2, 67722-87-6; **26** isomer 1, 67722-88-7; **26** isomer 2, 67722-89-8; **27** isomer 1, 67722-90-1; **27** isomer 2, 67722-91-2; **28** isomer 1, 67722-92-3; **28** isomer 2, 67722-93-4; **29** isomer 1, 67722-94-5; **29** isomer 2, 67722-95-6; acetyl chloride, 75-36-5; heptadecanoyl chloride, 2528-61-2; decanoyl chloride, 112-13-0; butanoyl chloride, 141-75-3; 2-methylpropanoyl chloride, 79-30-1; 2,2-dimethylpropanoyl chloride, 3282-30-2; benzeneacetyl chloride, 103-80-0; myristoyl chloride, 112-64-1; stearoyl chloride, 112-76-5; benzoyl chloride, 98-88-4; chloroacetyl chloride, 79-04-9; 3-bromopropanoyl chloride, 15486-96-1; trifluoroacetyl chloride, 354-32-5.

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Model Studies of the Thioindigo Chromophore

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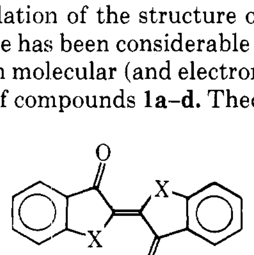
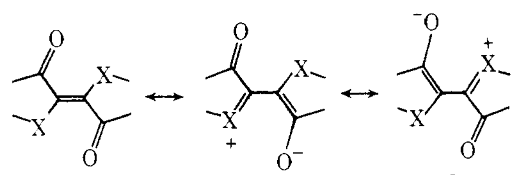
X-ray diffraction methods have been used to study the crystal structures of *trans*-$\Delta^{2,2'}$-bis(4,4-dimethylthiolan-3-one) (4) and *trans*-3,4-bis(methylthio)-3-hexene-2,5-dione (6) as model compounds for the thioindigo chromophore. The central region of the thiolanone molecule (4) and the upper SC=CC=O half of 6 are reasonably planar, but CH_3. . .CH_3 nonbonded interactions have produced considerable out-of-plane distortions of the CH_3C=O and CH_3S groups in the lower part of 6. Bond lengths reflect some conjugative interactions, but involvement of the C=O groups is small. It is concluded that the extent of merocyanine-like interactions between sulfur and oxygen (viz., SC=CC=O ↔ S^+=CC=CO^-) is small and that the ground state structure can be represented best as a hybrid of structures SC=CC=O ↔ ^+S=CC^-C=O.

Since the elucidation of the structure of indigo (**1a**) and its synthesis,[1] there has been considerable interest in the relationship between molecular (and electronic) structure and color in the class of compounds **1a–d**. Theories advanced on



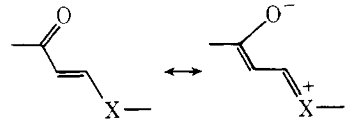
1a, X = NH; λ_{max} 588 nm
b, X = S; λ_{max} 541 nm
c, X = Se; λ_{max} 558 nm
d, X = O; λ_{max} 410 nm

the relationship between structure and color[2] generally were unable to rationalize how the deep color of the indigo dyes is related to the relatively compact mesomeric system. Klessinger and Luttke,[4] however, have shown with HMO and PPP calculations that the 10 π-electron system embodied in **2** should have the same spectroscopic properties as the indigo dyes. According to their work, the ground state electronic structures of the indigos can be represented as a resonance hybrid of canonical forms **2a–c**, similar to the merocyanines



2a 2b 2c

(**3**).[5] Accordingly, removal of the benzene rings in **1** should not



3a 3b

change the basic characteristics of the electronic transitions and other properties typical of the indigos. This idea has been tested by the synthesis of **4**,[6] which has the same planar configuration as the thioindigo chromophore. The compound has similar chemical properties to thioindigo (**1b**),[6–8] and the long

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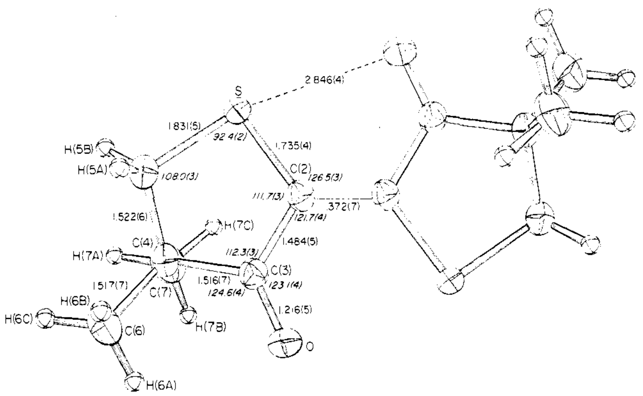
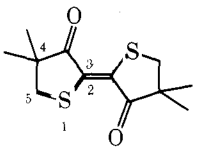
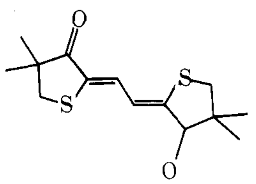


Figure 1. Bond lengths (Å), angles (deg), and estimated standard deviations (in parentheses) for *trans*-$\Delta^{2,2'}$-bis(4,4-dimethylthiolan-3-one) (**4**). The C, O, and S atoms are drawn as 50% ellipsoids; H atoms are illustrated as 0.1 Å radius spheres. Heavy atom distances and angles not included in the drawing are the following: C(3)–C(7), 1.540 (9) Å; C(3)–C(4)–C(5), 105.5 (4)°; C(3)–C(4)–C(6), 111.3 (4)°; C(3)–C(4)–C(7), 106.8 (4)°; C(5)–C(4)–C(6), 111.6 (4)°; C(5)–C(4)–C(7), 109.6 (4)°; C(6)–C(4)–C(7), 111.7 (4)°. Bond lengths and angles involving the hydrogen atoms are given in tables as supplementary material.

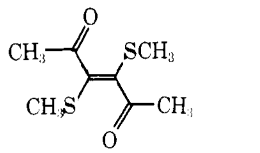


4

wavelength absorption maximum is only shifted from 546 nm in **1b** to 458 nm ($HCCl_3$) in **4**, despite the reduction in the conjugated system from 22 to 10 π electrons. The structure of **4** might also be best represented as a resonance hybrid of forms like **2a–c**, although the spectral differences between the indigos and merocyanines, viz., the hypsochromic shift accompanying the introduction of a second C=C between the two five-membered rings as in **5**[6,7] and by distortion around



5



6

the C=CS and C=CC=O moieties as in **6**,[8,9] suggest that the description of the electronic structures of indigos as cross-conjugated merocyanines might be too simple a picture.

In order to obtain more information on the ground state structures of indigo model compounds, we have undertaken the X-ray crystallographic investigation of *trans*-$\Delta^{2,2'}$-bis(4,4-dimethylthiolan-3-one) (**4**) and *trans*-3,4-bis(methylthio)-3-hexene-2,5-dione (**6**). If the picture of the ground state as a hybrid of forms **2a–c** is valid, we would expect to find a shortening of the C=CC=O and C=CS single bonds and a lengthening of C=C and C=O, similar to the changes observed in compounds with typical merocyanine characteristics (vide infra). The X-ray structures of indigos **1a–c** have been investigated,[3,10,11] but the uncertainties in the reported bond lengths are too large for meaningful conclusions to be drawn.

Discussion

An ORTEP-II[12] drawing of **4**[13] containing bond lengths and angles is shown in Figure 1. The unique crystallographic unit consists of one 4,4-dimethylthiolan-3-one half (C_6H_8SO); the two halves of a molecule are related by a crystallographic (and molecular) center of symmetry between C(2) and C(2′). The mean planes of the two halves are parallel, but they deviate slightly from perfect coplanarity with a distance, for example, of 0.035 Å between the planes S–C(2)–C(3) and S′–C(2′)–C(3′). The least-squares plane through all six of the central atoms gives an average out-of-plane distance of 0.004 Å.

The thiolanone ring is somewhat puckered; with S–C(2)–C(3) as a reference plane, C(4) is 0.207 Å below the plane and C(5) is 0.320 Å above (Table I). In the vicinity of C(4), the five-ring pucker is clearly reflected in the out-of-plane distances of the two methyl groups; C(6) is 0.524 Å above and C(7) is 1.726 Å below the five atom least-squares plane. The carbonyl oxygen atom is 0.105 Å out of the S–C(2)–C(3) plane. This puckering of the five-membered ring also can be described in terms of angles between the planes of the central six atoms [plane 1: S–C(2)–C(3)–C(3′)–C(2′)–S′], the carbonyl group [plane 2: C(2)–C(3)–C(4)–O], and the sulfur moiety [plane 3: C(2)–C(5)–S]. The interplanar angles are $\frac{1}{2}$ = 8.1°, $\frac{1}{3}$ = 9.5°, and $\frac{2}{3}$ = 15.0°.

The effect of releasing the conformational constraints imposed by the five-membered rings in **4** can be clearly seen in the structure of **6** (Figure 2). The central, double-bond containing portion of the molecule is approximately planar with an average out-of-plane distance of 0.036 Å for the six atoms (Table II), whereas the CH_3S and CH_3C=O groups have undergone substantial conformational changes, from the approximately planar **4**, to relieve $CH_3\cdots CH_3$ nonbonded interactions. It is interesting that the $CH_3\cdots CH_3$ contacts on the right and left sides of the molecule are virtually identical and that the major out-of-central-plane deviations occur in the bottom half of the molecule. The upper SC=CC=O unit remains more-or-less planar, and the resulting S(2)···O(1) distance of 2.76 Å is very close to the corresponding 2.85 Å contact in **4**. Both of these distances are appreciably smaller than the typical S···O van der Waals contact of 3.2 Å; the lower S(1)···O(2) distance is 3.57 Å. With reference to the central S(C)C=C(C)S planes, the out-of-plane distances are −0.317 and 1.130 Å, respectively, for O(1) and O(2) in **6** and 0.108 Å for O in **4**. Interplanar angles for various groups of atoms in **6** are reported in Table III; with respect to the central six-atom plane in **6**, the interplanar angles are 64.8 and 88.2°, respectively, for the lower CSC and CC(=O)C groups and 12.9 and 25.0°, respectively, for these groups in the upper half of the molecule.

In the SC=CC=O unit of **4**, the C=O and C—C distances of 1.216 and 1.484 Å, respectively, are typical for these kinds of connections in the absence of π-bond conjugative effects.

Table I. Least-Squares Planes and Deviations (Å) for 4

atoms	plane 1	plane 2	plane 3
S	0.0[a]	−0.125[a]	−0.002[a]
C(2)	0.0[a]	0.032[a]	0.009[a]
C(3)	0.0[a]	0.093[a]	−0.002[a]
C(4)	−0.207	−0.202[a]	−0.227
C(5)	0.320	0.201[a]	0.299
C(6)	0.524	0.566	
C(7)	−1.726	−1.724	
O	0.105	0.307	−0.108
S′[b]	−0.035		0.002[a]
C(2′)[b]	−0.035		−0.009[a]
C(3′)[b]	−0.035		0.002[a]

[a] Used for plane definition. Plane 1: $-4.8321x + 3.8076y + 7.9008z = 6.8935$. Plane 2: $-4.8065x + 3.4902y + 8.6266z = 7.2625$. Plane 3: $-4.9382x + 3.7691y + 7.9578z = 0.0$. [b] Related by center of symmetry.

Table II. Least-Squares Planes and Deviations (Å) for 6

atoms	deviations	atoms	deviations
S(1)	−0.025[a]	C(5)	0.052[a]
S(2)	−0.027[a]	C(6)	−1.226
C(1)	0.673	C(7)	−1.629
C(2)	0.055[a]	C(8)	0.362
C(3)	−0.038[a]	O(1)	−0.317
C(4)	−0.018[a]	O(2)	1.130

[a] Used for plane definition. Plane: $8.8917x + 3.0625y - 8.205z = 1.1200$.

Table III. Interplanar Angles (deg) for 6[a]

plane	plane 2	3	4	5
1	25.0	88.2	64.8	12.9
2		67.0	81.7	33.7
3			61.3	82.9
4				52.0

[a] Plane 1: C(2)–C(3)–C(4)–C(5)–S(1)–S(2). Plane 2: C(1)–C(2)–C(3)–O(1). Plane 3: C(4)–C(5)–C(6)–O(2). Plane 4: C(3)–C(7)–S(1). Plane 5: C(4)–C(8)–S(2).

The corresponding values, for example, in two α,β-unsaturated ketones are C═O = 1.204 Å and C—C = 1.478 Å in benzylideneacetophenone[14] and C═O = 1.228 Å and C—C = 1.490 Å in (p-methoxybenzylidene)acetophenone.[15] The C—C═O distances in 4 suggest that any merocyanine-like resonance interaction with the SC═C unit must be sufficiently small not to have an observable impact on the ground state structure. In contrast to these normal values, the C═C distance of 1.372 Å is significantly longer than the standard ethylenic value of 1.337 Å,[16] and the C—S distance of 1.735 Å is typical of linkages with substantial amounts of π-bond character. For example, the distance is about one-third closer to the 1.717 Å value in thiophene[17] than to the standard single C(sp^2)—S length of ca. 1.78 Å.[18] The overall pattern of SC═CC═O bond lengths does not show the merocyanine characteristics exemplified in 7 and 8 (Table IV), which arise from substantial contributions of structures similar to **3b** (ca. 30% in 7 and 24% in 8) to the ground state hybrids.

In the structure of **6**, one sees a balance between the loss of resonance energy incurred by distortion of the central mesomeric system and the release of steric strain energy. Various bond- and angle-twisting modes and out-of-plane distortions have alleveated the $CH_3 \cdots CH_3$ nonbonded interactions on the right and left sides of the molecule. As already concluded from spectroscopic evidence, the molecule is divided into a conjugated, almost planar, merocyanine-like upper part of S(2)—C(4)═C(3)—C(2)═O(1) and a noninteracting lower part containing methylthio and carbonyl groups; the arrangement of the CH_3C═O and CH_3S groups in the upper and lower halves of the molecule is in accord with existing ideas on the compound's conformational mobility.[9] The upper C—S distance of 1.748 Å is significantly shorter than the 1.78 Å C(sp^2)—S distance,[18] while the lower C—S bond length appears normal. The central C═C is slightly elongated. A comparison of the upper C(2)—C(3) = 1.486 Å and C(2)═O(1) = 1.218 Å distances with the lower values of C(4)—C(5) = 1.512 Å and C(5)═O(2) = 1.209 Å indicates that there may be a small contribution from a canonical form similar to **3b** in the upper half of the molecule. While the C(2)—C(3) and C(2)═O(1) lengths are virtually identical with the C—C═O values in **4**, differences between the S—C═C distances in the two molecules suggest that mesomeric contributions of the $^+$S═CC$^-$ and $^+$S═CC═S$^-$ types may be significant in **4**.

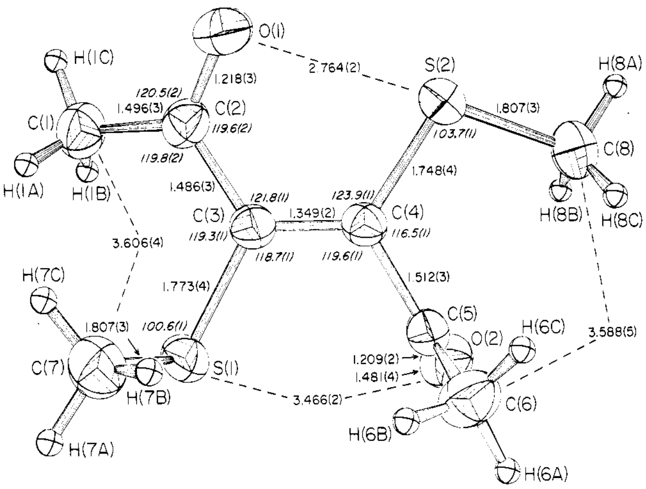
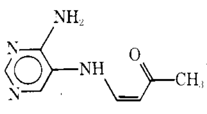
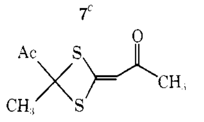


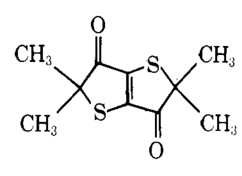
Figure 2. Bond lengths (Å), angles (deg), and estimated standard deviations (in parentheses) for *trans*-3,4-bis(methylthio)-3-hexene-2,5-dione (**6**). The C, O, and S atoms are drawn as 45% ellipsoids; H atoms are illustrated as 0.1 Å radius spheres. Heavy atom angles not included in the drawing are the following: C(4)–C(5)–C(6), 117.7 (2)°; C(4)–C(5)–O(2), 119.5 (2)°; C(6)–C(5)–O(2), 122.8 (2)°. Bond lengths and angles involving the hydrogen atoms are given in tables as supplementary material.

Table IV. Bond Lengths (Å) for XC═CC═O Units

compd	X—C	C═C	C—C	C═O
4	1.735 (4)[a]	1.372 (7)	1.484 (5)	1.216 (5)
6	1.748 (4)[a]	1.349 (2)	1.486 (2)	1.218 (3)
	1.773 (4)	1.349 (2)	1.512 (2)	1.209 (2)
 7[c]	1.37 (1)[b]	1.37 (1)	1.41 (1)	1.26 (1)
 8[d]	1.718 (6)[a] 1.786 (5)	1.377 (7)	1.441 (8)	1.271 (7)

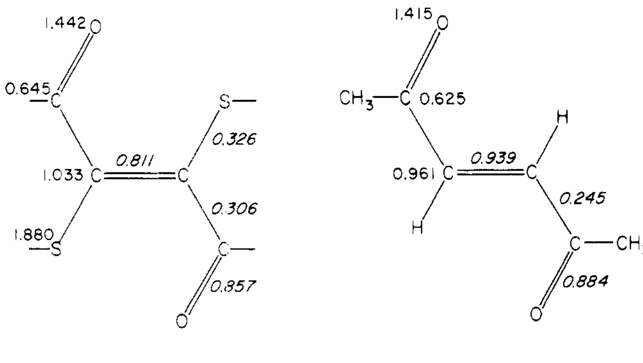
[a] X = S. [b] X = N. [c] J. Silverman and N. F. Yannoni, *Acta Crystallogr.*, **18**, 756 (1965). [d] J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Am. Chem. Soc.*, **90**, 5800 (1968).

Crystal packing diagrams of thioindigo[11] and model compounds **4**, **6**, and **9**[19] were studied to determine if the pattern



9

of intermolecular contacts in thioindigo would be emulated in the three model structures. Our analysis, which was limited to contacts less than 4 Å and centered on S and O, found three patterns in the four structures and very few similarities. The thioindigo contacts reflected the smallest degree of intermolecular interactions; they were limited to a pair of 3.73 Å S···O approaches between molecules related by a center of symmetry. In **9**, each sulfur is involved in 3.47 Å S···O and 3.89 Å S···S contacts to a *c*-glide related molecule. A similar arrangement is found between center of symmetry related molecules of **6**, with pairs of 3.38 Å S(1)···O(1) and 3.85 Å



2 14

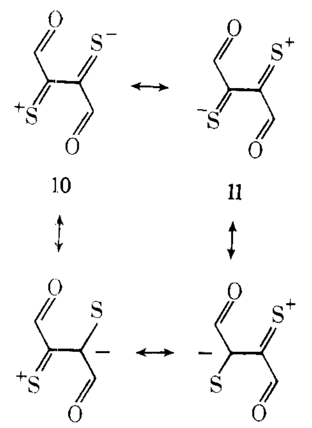
Figure 3. PPP π-electron densities and bond orders (slanted values) in 2 and 14.

S(1)···S(1) contacts. While these interactions involve the methylthio and acetyl groups in the twisted lower section of the molecule, the conjugated upper section is involved in a single 3.60 Å S(2)···S(2) contact to another center related molecule. In **4**, these interactions are limited to a single 3.77 Å S···S contact between *c*-glide related molecules. There are no contacts to O.

We have used Pauling's equation (eq 1),[20] which relates bond length (d) to standard single (d_s) and double (d_d) bond lengths and bond number (n), to estimate the contributions of canonical forms **2a–c** (X = S) and **10–13** to the resonance hybrid of **4**.

$$d = d_s - (d_s - d_d)\frac{1.84(n-1)}{0.84n + 0.16} \qquad (1)$$

The limiting bond distances taken for the calculations were the following: C—C, d_s = 1.504 Å, d_d = 1.334 Å;[21] C—S, d_s = 1.804 Å, d_d = 1.570 Å;[22] C—O, d_s = 1.411 Å, d_d = 1.209 Å.[23]



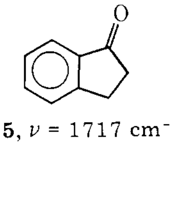
10 11

12 13

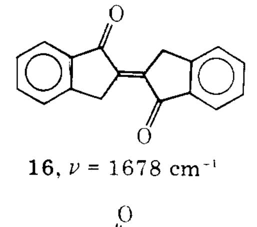
A short computer program was written to (a) form all possible combinations of the percent contributions of the possible contributing structures (Table V), (b) evaluate n from the percent contributions, (c) compute d's from n's, and (d) evaluate the optimum set of percent contributions from the minimum in the function $\sum^i(d_{\text{exptl},i} - d_{\text{calcd},i})^2$. In Table V, the middle column lists the optimum contributions of essentially four contributing structures (actually one single plus three pairs of structures), while the right-most results were obtained with the elimination of canonical forms **10** and **11**, the two structures which imply sulfur d orbital interactions.[24] Both columns illustrate that the contribution of the dipolar, merocyanine-like structures **2b** and **2c** is small, amounting at most to about 14%. Interestingly, the most important of the minor contributions is from structures **12** and **13**, the dipolar ene–sulfide mesomeric forms. The ene–sulfide contribution amounts to about twice that of the merocyanine value, with the elimination of forms **10** and **11**.

These results contrast with the generally accepted view derived primarily from PPP and Hückel calculations,[25] in which the ground state π-electron distribution is represented by a resonance hybrid containing substantial contributions from dipolar, merocyanine-like structures **2b** and **2c**. However, a different picture emerges if one looks at the π-electron distribution in both **2** (X = S) and a compound like diacetylethylene (**14**) and not just at **2** alone. The PPP data[26] in Figure 3 and Table VI show that the introduction of two electron-donating sulfur atoms into the basic diacetylethylene molecule does not result in a large amount of charge transfer from sulfur to oxygen in the ground state. The C═O and C—C distances are predicted to undergo changes of +0.006 and −0.012 Å, respectively, from **14** to **2**. The largest bond length change of +0.025 Å, predicated for C═C, is close to the ca. 0.03 Å difference between the observed C═C in **4** (1.372 Å) and the standard ethylenic value (ca. 1.34 Å).

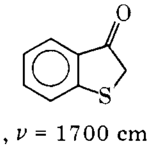
The absence of a substantial interaction of the heteroatom with the carbonyl group can also be illustrated with the infrared C═O stretching bands for compounds **15–17** and **1b**. The 39 cm⁻¹ shift in the carbonyl frequency from indanone **15** to **16** is virtually identical with the 44 cm⁻¹ difference be-



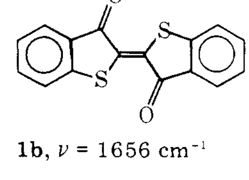
15, ν = 1717 cm^{-1}



16, ν = 1678 cm^{-1}



17, ν = 1700 cm^{-1}



1b, ν = 1656 cm^{-1}

Table V. Resonance Structure Contributions, Observed and Calculated Bond Lengths, and Bond Numbers[a] for 4

structure	contribution, %	contribution, %
2a	66	64
2b + 2c	14	13
10 + 11	4	0[b]
12 + 13	16	23

bond	obsd, Å	calcd, Å	bond number	calcd, Å	bond number
S—C	1.735	1.733	1.19	1.737	1.18
C═C	1.372	1.371	1.66	1.374	1.64
C—C	1.484	1.483	1.07	1.485	1.06
C═O	1.216	1.217	1.93	1.216	1.93

[a] The bond numbers for formal single and double bonds are, respectively, 1 and 2. [b] Fixed at 0%.

Table VI. Comparison of PPP Data for 2 and 14

	14	2		
λ_{max} (obsd), nm	221[a]	450[a]		
λ_{max} (calcd), nm	226	448		
bond	bond order (p)		Δp	Δ,[b] Å
C═C	0.939	0.811	0.128	+0.025
C—C	0.245	0.306	0.061	−0.012
C═O	0.884	0.857	0.027	+0.006

[a] In cyclohexane. [b] With bond order–bond length relationships from ref 22 and 23.

Table VII. Atomic Fractional Coordinates for *trans*-$\Delta^{2,2'}$-Bis(4,4-dimethylthiolan-3-one) (4)[a]

atom	*x*	*y*	*z*
S	1.0021 (1)	1.2882 (2)	0.86459 (9)
O	1.2354 (3)	0.9769 (7)	1.1706 (3)
C(2)	1.0426 (4)	1.0812 (8)	0.9891 (4)
C(3)	1.1867 (4)	1.0915 (8)	1.0723 (4)
C(4)	1.2653 (4)	1.2503 (9)	1.0176 (4)
C(5)	1.1659 (4)	1.4379 (9)	0.9331 (4)
C(6)	1.3819 (6)	1.377 (1)	1.1206 (6)
C(7)	1.3121 (5)	1.078 (1)	0.9369 (6)
H(5A)	1.159 (5)	1.59 (1)	0.982 (5)
H(5B)	1.190 (5)	1.50 (1)	0.867 (5)
H(6A)	1.431 (6)	1.25 (1)	1.182 (6)
H(6B)	1.343 (7)	1.52 (1)	1.175 (6)
H(6C)	1.430 (6)	1.49 (1)	1.096 (5)
H(7A)	1.366 (5)	1.17 (1)	0.902 (5)
H(7B)	1.362 (7)	0.94 (1)	0.984 (6)
H(7C)	1.226 (6)	0.99 (1)	0.876 (5)

[a] Estimated standard deviations are in parentheses.

tween these bands in **17** and thioindigo **1b**. The lowering of the carbonyl frequency from **17** to **1b**, which has been interpreted as evidence for a mesomeric interaction between S and C=O, actually originates in the **15** to **16** transformation, and it is only slightly effected by the presence of sulfur.

Conclusions

In the thioindigo chromophore **4**, the degree of interaction between sulfur and oxygen typified by resonance forms **2b** and **2c** is small, and there seems little reason to classify thioindigo as a merocyanine. The ground state structure can best be depicted, in terms of the valence bond structures most familiar to chemists, as a hybrid of structures **4**, **12**, and **13**.

Experimental Section

X-ray Crystallographic Study of *trans*-$\Delta^{2,2'}$-Bis(4,4-dimethylthiolan-3-one) (4). The compound was prepared by the method of Hermann and Luttke.[6] Recrystallization from ethanol gave light orange plates with the following crystal data: $C_{12}H_{12}S_2O_2$; M_r 252.4; monoclinic; $P2_1/c$; a = 10.911 Å; b = 5.397 Å; c = 11.560 Å; β = 113.33°; ρ(measd) = 1.36 g cm^{-3} (in CCl_4–C_6H_6); ρ(calcd) = 1.34 g cm^{-3}; Z = 2. Unit cell parameters were determined from oscillation and $h0l$ Weissenberg pictures (Ni-filtered Cu Kα radiation, λ = 1.5418 Å) calibrated with NaCl (a = 5.6396 Å).

The diffraction intensities were recorded by the multiple film pack Weissenberg method with Ni-filtered Cu Kα radiation for the $h0l$ – $h5l$ levels with a 0.15 × 0.3 × 0.3 mm crystal and for the $hk0$ – $hk3$ levels with a 0.2 × 0.3 × 0.3 mm crystal. The integrated intensities were measured with a Joyce-Deeley flying-spot densitometer, and the interlevel scale factors were calculated with the algorithm of Fox and Holmes.[27] Unobserved reflections were assigned an intensity equal to the minimum observed intensity on the particular level. The numbers of unique data were 1020 observed and 200 unobserved (excluding space group absences). The structure was solved in a routine manner with the direct methods program PHASER.[28]

The structure refinement used the full matrix of the normal equations. Anisotropic temperature factors were applied to carbon, oxygen, and sulfur, and the hydrogen atoms (initially located in a difference map) were refined with isotropic terms. The final refinement cycles used a Hughes-type[29] of weighting scheme (w = 1 for $F \le 24$, $w = (24/F)^2$ for $F > 24$) and minimized the function $\sum w(F_o - F_c)^2$. The unobserved reflections were included in the calculations only in those cases in which F_c calculated greater than the threshold value of F_o. This amounted to 56 data during the last cycle. The calculations included a correction for secondary isotropic extinction with eq 22 in ref 30. The value of r^* was 0.04 (5). The final R and weighted R factors $[(\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2}]$ were 0.060 and 0.075, respectively.

Atomic scattering factors for carbon, oxyten, and sulfur were taken from ref 31 and for hydrogen from ref 32.

The atomic coordinators are given in Table VII. A thermal parameter table is included as supplementary material.

Table VIII. Atomic Fractional Coordinates for *trans*-3,4-Bis(methylthio)-3-hexene-2,5-dione (6)[a]

atom	*x*	*y*	*z*
S(1)	0.41602 (5)	0.30215 (6)	0.41913 (4)
S(2)	0.09072 (5)	0.50457 (7)	0.14244 (4)
O(1)	0.3307 (1)	0.7196 (2)	0.3417 (1)
O(2)	0.1673 (1)	0.1697 (2)	0.1357 (1)
C(1)	0.3902 (2)	0.0679 (3)	0.2186 (2)
C(2)	0.2734 (2)	0.1830 (2)	0.2104 (1)
C(3)	0.2895 (2)	0.3211 (2)	0.2906 (1)
C(4)	0.2183 (2)	0.4671 (2)	0.2656 (1)
C(5)	0.2505 (2)	0.6116 (2)	0.3459 (1)
C(6)	0.1774 (3)	0.6169 (3)	0.4244 (2)
C(7)	0.3470 (3)	0.1308 (3)	0.4758 (2)
C(8)	0.0589 (3)	0.7301 (3)	0.1447 (2)
H(1A)	0.411 (3)	−0.002 (4)	0.275 (3)
H(1B)	0.470 (4)	0.122 (4)	0.232 (3)
H(1C)	0.375 (3)	0.000 (4)	0.154 (3)
H(6A)	0.206 (3)	0.708 (4)	0.474 (2)
H(6B)	0.191 (3)	0.517 (4)	0.465 (2)
H(6C)	0.086 (3)	0.625 (3)	0.386 (2)
H(7A)	0.408 (3)	0.106 (3)	0.546 (2)
H(7B)	0.264 (3)	0.165 (3)	0.484 (2)
H(7C)	0.334 (3)	0.033 (4)	0.433 (2)
H(8A)	−0.006 (2)	0.755 (3)	0.076 (2)
H(8B)	0.142 (3)	0.788 (4)	0.156 (2)
H(8C)	0.020 (3)	0.759 (4)	0.201 (2)

[a] Estimated standard deviations are in parentheses.

The intensity work was done at the University of California in Santa Cruz, California, and preliminary calculations were done at the university on an IBM 360/40 computer. The final calculations were done on a UNIVAC 1108 at the University of Maryland's Computer Science Center with the XRAY72 system of programs.[33]

X-ray Crystallographic Study of *trans*-3,4-Bis(methylthio)-3-hexene-2,5-dione (6). The compound was prepared according to the method of Hermann and Luttke.[9] Recrystallization from petroleum ether gave light yellow blocks with the following crystal data: $C_8H_{12}S_2O_2$; M_r 204.3; monoclinic; $P2_1/c$; a = 10.473 (3) Å; b = 7.868 (1) Å; c = 13.198 (4) Å; β = 109.63 (1)°; ρ(measd) = 1.322 g cm^{-3} (in H_2O–KI); ρ(calcd) = 1.325 g cm^{-3}; Z = 4. The unit cell parameters and all intensity measurements were made with a Picker FACS-I computer-controlled diffractomer with Mo radiation diffracted from a highly oriented graphite crystal monochromator (Kα λ = 0.71069 Å). The cell constants were determined by the method of least squares from the Bragg angles of 15 reflections manually centered at $\pm 2\theta$.

The diffraction intensities were measured on the diffractometer with the θ–2θ scan method, with a 2θ scan rate of 2°/min, and with two 20-s backgrounds. A crystal fragment cut to ca. 0.24 × 0.36 × 0.36 mm was mounted parallel to b in a thin-walled glass capillary, which was necessary because the material sublimed extremely readily (mp 45 °C) even at room temperature and atmospheric pressure. Three standard intensities were counted at 100 reflection intervals to monitor intensity fluctuations. Data scale factors calculated from these standard measurements showed a maximum change from start to finish of approximately 10%. A total of 3333 unique reflections (excluding space group absences) were measured to a 2θ maximum of 65°. A total of 2370 of these intensities were more than $3\sigma(I)$ above background. The structure was solved in one computer pass with the XRAY72's[33] direct methods subprogram PHASE.

The least-squares structure refinement used anisotropic temperature factors for carbon, oxygen, and sulfur and isotropic terms for hydrogen (initially located in a difference map). The weighting scheme used in the final refinement cycles was w = [0.17/MAX ($\sigma(F_o)$, $0.0061F_o$, 0.17)]^2. The function gave unit weights to F_o's in the 6 to 28 range and down-weighted F_o's < 6 and > 28. Reflections were included in the refinement only in those cases where I_c was greater than $3\sigma(I_o)$, amounting to 2689 data in the last cycle. The refined secondary isotropic extinction factor $(r^*)^{30}$ was 0.0510 (8). The final R and weighted R factors were 0.041 and 0.039, respectively.

Atomic scattering factors for carbon, oxygen, and sulfur were taken from ref 31 and for hydrogen from ref 32.

The final atomic coordinates are given in Table VIII. A table of thermal parameters is included as supplementary material.

All of the crystallographic calculations were done with the XRAY72[33] system of programs on a UNIVAC 1108 computer.

Acknowledgment. The crystallographic calculations were supported through the facilities of the Computer Science Center, University of Maryland. We wish to thank Professor W. Luttke, University of Gottingen, for many helpful discussions.

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Supplementary Material Available: Tables of temperature factors and bond lengths and angles involving hydrogen atoms (4 pages). Ordering information is given on any current masthead page.

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Absolute Configuration of (+)-Methyl 8-Methyl-8-azabicyclo[3.2.1]oct-2-ene-3-carboxylate

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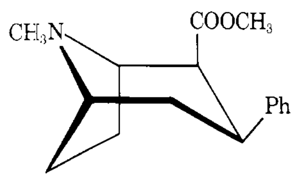
The absolute configurations of the enantiomers of ester **2** were needed in order to establish the configurations of a narcotic antagonist (**3**) and a hypoglycemic agent (**4**), wherein the biological activity resided in a single enantiomer. Ester **2** was resolved via its dibenzoyltartrate salts and its (+)-form was converted to ketone **8**, a compound that was also prepared from cocaine which is known to have a 1*R* configuration. Therefore, (+)-**2** has the 1*R* configuration.

Earlier a tropane molecule carrying an equatorial phenyl group on carbon 3 and an axial carbomethoxy group on carbon 2 (**1**) was shown to be a powerful CNS stimulant, the activity



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residing in only one enantiomer.[1] Since the ester was prepared from (−)-anhydroecgonine methyl ester derived from cocaine, the absolute configuration was known.

Concurrently with the present work another aryltropanecarboxylic ester (**3**) is being reported which is a narcotic antagonist[2] while a third such ester (**4**) is a hypoglycemic agent.[3] In each of these cases only one enantiomer is active and they are derivable (separately) from the enantiomeric forms of **2** (see eq A and B). The absolute configuration of narcotic antagonist **3** is of particular interest since the compound constitutes a new structural form displaying this broadly studied biological activity. Assignment of absolute configurations to **3** and **4** hinges upon determination of the absolute configuration of one of the enantiomers of **2**. The present paper presents proof for the absolute configuration of (+)**2**.

Cocaine is known to have a 1*R* configuration.[4] The pattern for the present proof involved conversion of a known derivative of cocaine [(−)-**5**][5] to ketone **8** which could also be derived from **2**. (−)-**5** was treated with ethyl chlorocarbonate and the resulting urethane **6** was oxidized by Jones' reagent. Equilibration of the α-methyl ketone so formed (**7**) with sodium methoxide in methanol then provided **8** (1*R* configuration, $[\alpha]_D$ −24.4°). The remaining problem involved conversion of **2** to **8**.

